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2,456,520, on January 30, 2004, by **HUBERT PATROVSKY**, for "Nitriding Method for  
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O P I C  C I P O

**Abstract:**

A method for improving the surface characteristics of Cobalt chromium alloys by plasma nitriding. By creating a glow discharge around the parts with selective gases at partial pressures a compound layer is formed at the surface beneficial for wear applications. A further benefit is an increase in the load bearing capacity of the surface as compared to standard material.

## NITRIDING METHOD FOR IMPROVING SURFACE CHARACTERISTICS OF COBALT-CHROMIUM BASED ALLOYS

### Field of Invention

The present invention relates to cobalt-chromium based alloys and particularly to a method of surface treatment of such alloys, beneficial for surface hardness, smoothness and corrosion and wear resistance, while meeting the criteria of at least equivalent fatigue strength.

### Background

Cobalt-chromium based alloys, including cobalt-chromium molybdenum alloys are known in the art and the properties of such alloys make them suitable for selection in many specialized types of applications, requiring heat resistance, high surface hardness, wear resistance, high surface smoothness, mechanical strength, resistance to surface degradation and biocompatibility.

Many applications will be known for such alloys, a non-exhaustive list including aircraft and steam turbines, gas turbines, reciprocating engines, metal processing, medical applications and devices, space vehicles, heat treatment equipment, nuclear power systems, chemical and petrochemical industries, pollution control equipment, metal processing mills and coal gasification and liquefaction systems.

When evaluating an alloy for suitability in an application such as described above, the skilled person must take many technical considerations into account, such as formability, strength, creep resistance, fatigue strength, surface smoothness, hardness and stability. N.S. Stroloff, in *Wrought and P/M Super Alloys, Specialty Steel and Heat-Resistant Alloys*, pages 950 to 980 discusses the interplay between composition, micro structure, consolidation method, mechanical properties and surface stability, which article is incorporated herein by reference. Accordingly, the particular application for the alloy being important, a method suitable for improving surface characteristics of a cobalt-chromium alloy must not otherwise result in unacceptable changes to other properties of the alloy, such as fatigue strength.

A particular limitation of cobalt chrome based alloys is that the metal morphology lends itself to the formation of carbides at the finished surface of the metal. As well, grains at or near the surface may present grain boundaries which intersect with the

surface, thus presenting surface discontinuities, defined by the edges of adjacent grains. Wear of surfaces of cobalt-chromium based alloys will result in exposure of carbide particles. Under conditions of articulating or sliding motion or relative motion of opposing abutting surfaces, where one of the surfaces is composed of a cobalt-chromium alloy as aforesaid, with another surface which may be made of a relatively softer or more friable material, this will result in undesirable wear conditions on the softer surface due to the hard particles or discontinuities on the opposing surface. This may give rise to undesirable results, associated not only with the damage to the opposing softer, more friable surface, but also to the generation of particles arising from the damaged surface. Such generated damage particles may be undesirable in many circumstances. For example, in prosthetic devices which involve relative movement of weight bearing surfaces, where one of the surfaces may be composed of a cobalt-chromium metal alloy and the other surface of a softer, more friable material, wear on the softer surface will result in wear particles being released, which may pose a health hazard to a patient and a compromise to biocompatibility. In such circumstances, there is a real need for improving not only surface hardness but also surface smoothness of the cobalt-chromium alloy surface, to minimize the aforesaid type of wear and the negative effects associated therewith.

Many processes are known for improving the surface hardness of cobalt-chromium alloys, to improve wear resistance of the cobalt-chromium components relative to opposing components. For example, improvement of surface hardness has been achieved by deposition of a titanium nitride coating on the surface of the cobalt-chromium alloy. This has also been achieved by various means of diffusion nitriding of cobalt-chromium surfaces. Known methods of surface hardening through diffusion nitriding, include gas nitriding, chemical salt bath nitriding and ion implantation methods.

Cobalt-chromium based alloys may be surface strengthened by nitrogen addition in the molten state or by nitrogen diffusion in the alloy in the solid state. Common methods encompass using a majority fraction of nitrogen gas in combination with a minority fraction of hydrogen and significantly smaller fractions of ammonia. Cobalt-chromium alloys which may be treated by such method include but are not limited to ASTM F-75 and ASTM F-799. However, such processes can lead to a significant increase in the nitrogen content present throughout the bulk alloy metal. Adding nitrogen in this manner has been found to create gross changes in the alloy, which

may be manifest as a significant reduction in the fracture toughness of the alloy. Such processing may also lead to hydrogen embrittlement and decarburization due to the presence of free hydrogen from the dissociated ammonia in the process. Carbon is a known element to increase hardness of alloys therefore loss of carbon from the chemical matrix of the alloy will reduce hardness for both the surface and bulk volume of a cobalt-chromium alloy.

U.S. Patent No. 5,308,412 of Shetty et al discloses gas nitriding in positive pressure with substantially pure nitrogen gas or ionized nitrogen. According to the disclosure of Shetty et al, the result is a hardened diffusion layer bounded by the surface and a substrate of cobalt-chromium alloy, enhancing the hardness and wear resistance of the surface of the alloy with minimal reduction in fatigue resistance. According to the disclosed process, there is prevention or minimizing of the formation of a chromium nitride compound layer on the surface due to apparent detrimental effects therein associated with purported increase in surface roughness and brittleness which lead to reduced wear resistance and a reduction of fatigue strength.

Gas, ion implantation and salt bath nitriding have all been attempted on cobalt-chrome alloys however all have their drawbacks. Ion implantation is a line of site process, therefore making uniformity of treatment extremely difficult if not impossible to achieve on complex geometries. Salt bath nitriding exposes the parts to excessive temperatures and gas nitriding causes hydrogen embrittlement and decarburization near the surface.

Accordingly, there is a need for a process to increase the surface hardness of cobalt-chromium based alloys while maintaining the equivalent or greater fatigue strength and increasing wear resistance.

It is an object of the present invention to provide a process which increases surface hardness while maintaining equivalent or greater fatigue strength and increasing wear resistance.

It is a further object of the present invention to provide a process as aforesaid which achieves a surface compound layer substantially comprising chromium nitride.

It is a still further object of the present invention to provide processes as aforesaid while providing control of the thickness of the surface layer and of the transition layer.

Control of the transition layer will assist in avoiding inter-granular precipitates, which may be detrimental to physical properties of the alloy, such as in the case of a casting.

A still further object of the present invention is the formation of a compound layer, which improves surface roughness, by subsuming surface carbide particles and boundary associated discontinuities.

A still further object of the present invention is to provide a process which avoids or minimizes the loss of carbon at or near the surface associated with other forms of nitriding, by introducing carbon in forms of a carbon precursor such as but not limited to methane (CH<sub>4</sub>) C<sub>2</sub>H<sub>2</sub>, NCCN and the like, which when cracked in the process provides elemental carbon. When introduced in the appropriate quantities, the concentration of carbon in the alloy being processed is maintained through an equilibrium.

A still further object of the present invention is a cobalt-chromium based alloy and any product made therefrom with increased surface hardness while maintaining equivalent or greater fatigue strength and increasing wear resistance, by processing of the alloy and/or product as aforesaid.

#### Summary of the Invention

The present invention relates to a process for enhancing the surface hardness of cobalt-chromium based alloys by creating a compound layer on the surface substantially comprising chromium nitride with other nitrides formed from other nitride forming elements such as molybdenum used in alloying, with cobalt still present in the compound layer but not in a nitrided form as cobalt does not normally form stable nitrides. In a further aspect, the present invention comprises a process as aforesaid, while controlling the transition layer.

A still further aspect of the present invention is a process as aforesaid wherein the compound layer provides a hard surface with improved wear resistance.

A still further aspect of the present invention is a process as aforesaid wherein the compound layer provides a hard surface with high wear resistance and a lower coefficient friction.

An advantage of the method of the present invention over deposited coating methods is that the surface of the cobalt-chromium alloy is thermo-chemically converted thereby avoiding adhesion related problems associated with deposited coating processes, as the formed compound layer is an integral part of the alloy and any part or component made of such alloy.

A still further aspect of the present invention is the formation of a compound layer which improves the surface roughness by subsuming surface carbides and discontinuities associates with grain boundaries. Subsequent polishing and buffing may further improve surface smoothness.

A still further aspect of the process of the present invention is a process for enhancing the surface hardness and smoothness of cobalt-chromium based alloys through exposure in a reaction vessel to a mixture of reaction gases at a partial pressure of less than one atmosphere within a temperature range of 250°C to 1000°C for a process time sufficient to create a compound surface layer.

A still further aspect of the present invention is a method as aforesaid wherein the reaction vessel utilizes a plasma glow discharge which may be pulsed or not as a media for the reaction.

A still further aspect of the present invention is a method as aforesaid wherein the mixture of gases comprises a carbon precursor such as but not restricted to CH<sub>4</sub> and/or NCCN and the like as examples, wherein elemental carbon is introduced in the appropriate quantity to maintain the concentration of carbon in the alloy being processed.

In a still further aspect of the present invention, there is a process as aforesaid wherein the transition layer is minimized in order to avoid inter-granular precipitates, which may be detrimental to the physical properties of the material in certain microstructures.

By the present invention for the creation of a surface compound layer, there is created a smooth surface which surround the carbide particles on the surface of the alloy with a layer which is equal to or harder than the carbide particles, thereby significantly increasing the overall wear hardness and smoothness of the surface of the cobalt-chromium alloy and any component made therefrom. The method of the

present invention achieves the aforesaid improvement in hardness and smoothness of the surface without significantly changing the metallurgical properties of the base metal cobalt-chromium alloy in such a part or component.

The formation of the compound layer serves to "seal" the grain boundaries where they intersect the surface, thereby eliminating discontinuities at the surface. It is known that certain forming processes of cobalt alloys may result in precipitation of hard compounds in the grain boundaries, which may present another possible source of debris for cause of abrasion. The formation of the compound layer as aforesaid may reduce the adverse affects associated with grain boundary wear mechanisms.

Another advantage associated with the process of the present invention is even and uniform application of a surface layer without regard to component geometry. As this is a thermo-chemical reaction, it is possible to control the exposure of surfaces to only those surfaces to be thermo-chemically converted. Further, the process being a thermo-chemical conversion may be carried out in a uniform manner. It is possible to control the conversion process by mechanical masking of any given surface, allowing for control of the areas on the surface of a particle component to undergo the thermo-chemical conversion associated with the process of the present invention.

The method of the present invention achieves a harder and smoother surface without significant change to the metallurgical properties of the base metal cobalt-chromium alloy. An additional merit of the current invention is the surface conversion of load bearing surfaces while maintaining the equivalent metallurgical properties including, but not limited to, fatigue strength. Yet another merit of the process of the present invention is the enhancement of surface hardness and smoothness while not limiting corrosion resistance properties of cobalt-chromium alloys.

#### **Brief Description of the Figures**

Figure 1 is a depiction of an exemplary replacement knee composed of a cobalt-chromium-molybdenum alloy.

Figure 2 is a micrograph depicting a grain boundary and the effect of covering the surface with a single phase compound layer.

Figure 3 depicts a surface with a two-phase compound layer.

Figure 4 further depicts a two-phase compound layer.

Figure 5 is a flow diagram of an exemplary process of the present invention.

**Detailed Description of the Invention**

The present invention relates to a method for enhancing the surface hardness and smoothness of a cobalt-chromium alloy, as well as wear resistance, while maintaining consistent metallurgical properties for the base metal. The method of the present invention imparts improved wear resistance properties. The present invention also comprises a component fabricated from cobalt-chromium based alloys with a compound surface layer. The process of the present invention allows control of the transition layer and a component or part of the present invention may also comprise such a transition layer, below the surface layer. The product or component also comprises a substrate metal of cobalt-chromium alloy.

The component is conditioned by hardening the surface of the cobalt-chromium base alloy metal by exposing all or part of a surface of a component or product made of such an alloy to a reaction gas, including nitrogen, at a pressure of less than 1 atmosphere and at a process temperature of about 250°C to 1000°C for a time sufficient to create a compound surface layer. The reaction gas may comprise of nitrogen or be a mixture of gases which in addition to nitrogen may optionally contain one or more carrier gases such as hydrogen optionally a surface activator such as argon and optionally a carbon precursor at the aforesaid temperature range. An electric potential is applied to create a plasma glow discharge. The process is carried out in a reaction vessel adapted for such purpose. Another gas may replace the hydrogen as the carrier gas, such as but not limited to helium or xenon.

Following the aforesaid process, a processed part or component may be further mechanically treated, such as by mechanical buffing, to improve the surface appearance.

Set out and discussed below are exemplary steps of the method of the present invention which is generally shown in Figure 5. The method of the present invention was conducted using an exemplary medical device, in particular, a prosthetic knee joint depicted schematically in Figure 1, composed of a cobalt-chromium molybdenum alloy ASTM F-75 on a support fixture. Other alloys in this family include,

but are not limited to, ASTM F-799, Stellite 21, Stellite 6B and Ultimet™. The exemplary prosthetic knee joint is of the type intended to be cemented to the distal end of the femur and to comprise a working surface intended for sliding contact with a tibial component (not shown). As typically used for such purpose, the tibial component comprises a platform (not shown) formed of an ultra high molecular weight cross-linked polyethylene. In use, the metal load bearing surfaces of the femoral component of Figure 1 articulate against the relatively softer aforesaid tibial platform of the tibial component.

The following are exemplary process steps for the process of the present invention:

Step 10: The part or component made of a cobalt-chromium based alloy, in particular the exemplary medical device as described above, to be treated is received either fully polished and colour buffed and in a clean condition or undergoes initial cleaning to remove any foreign material, such as finger prints, finishing or machine oils, polishing or buffing compounds or other materials encountered during manufacturing, shipping or handling of the components.

Step 20: Exemplary cleaning methods include, but are not limited to, ultrasonic cleaning, pressure washing or hand cleaning with and without soaps or surfactants, with and without a suitable solvent such as isopropyl alcohol, degreasing with commercially available degreasers and chemical etching with acids or caustic materials.

Step 30: The parts or components are then loaded into appropriate holding and/or masking fixtures to solidly support the parts or components to be treated and to optimize the exposure of the surfaces to be treated and mask any surfaces that are not intended to be treated. There is appropriate spacing to prevent hollow cathode defects and arcing from the glow discharge. As required, the fixtures also promote equal exposure of all of the components in a load to the process environment in the reaction vessel. The parts or components are loaded into a reaction vessel suitable for plasma nitriding and the reaction vessel is closed and sealed.

Step 40: To promote consistency of results, the reaction vessel is purged to remove environmental gases in the reaction vessel. Such gases may include oxygen, which is not conducive to the process. Typically, but without limitation, purging comprises the steps of evacuating the sealed vessel to a pressure of less than 1 atmosphere

and, typically, a pressure of less than 1 millibar (mbar), followed by the introduction of nitrogen to force remaining environmental gases out of the reaction vessel. Purging is typically conducted at a temperature between ambient temperature and approximately 300°C. The specific temperature during purging is determined experimentally and is influenced by the construction of the parts or components to be treated, including the size of the components and the thickness of the various sections of the parts or components and the sizes and weights of the parts or components making up the load in the vessel. for example, when processing a fully loaded reaction vessel containing a plurality of the exemplary prosthetic femoral knee components of Figure 1, the temperature of approximately 250°C has been found to be appropriate.

Step 50: An optional sputter step may be used, which may incorporate argon as a constituent in the gas mixture, to further clean contaminants and oxides from the surfaces thereby leaving an active surface to improve the subsequent pulse plasma nitriding steps.

Step 60 and 70: Following the aforesaid purging step or steps, the reaction vessel is evacuated to a pressure of less than 1 atmosphere and is backfilled to a partial vacuum with a reaction gas mixture suitable for the nitriding step or steps. The composition of the reaction gas can be varied for specific components or parts to be loaded in the vessel. The typical reaction gases are-nitrogen and a carrier gas such as hydrogen and may include argon and/or a carbon precursor such as methane. For example, a mixture of approximately 4-8% nitrogen, approximately 0-4% argon and approximately 94-98% hydrogen by volume at a pressure of less than 1 atmosphere has been found to be suitable for treatment of a full reaction vessel of femoral knee components as set out above. Additionally, trace amounts of methane may be added to the reaction gas to stabilize the carbon concentration in the treated parts or components. The reaction gas is introduced at a pressure of approximately 1-10 mbar when processing an exemplary load of femoral knee components. The nitride potential is designed to create the desired case depth and compound layer via nitrogen diffusion. For example, following introduction of the reaction gas, the temperature in the reaction vessel may be gradually increased and a pulsing voltage applied to the reaction gas to clean the exposed surface in preparation for the creation of a chromium nitride surface layer. For example, when processing an exemplary load of femoral knee components, the temperature may be raised at a

rate of approximately 150°C per hour from approximately 200°C to 500°C over a period not less than approximately two hours or more than five hours. A voltage applied to the reaction gas produces a plasma glow discharge surrounding the part or component in the reaction vessel. The skilled person will appreciate that the voltage to be applied must be suitable for the intended purpose and must therefore be of a suitable range. In the exemplary processing of femoral knee components, a pulsed voltage between 450 V and 500 V with an on/off time ratio (pulse/pause ratio) of approximately 2:5 was applied to the reaction gas. Examples of pulse/pause ratios for the present invention include 1:0-1:50. In the exemplary process for a load of prosthetic femoral knee joints, pulse/pause ratios of 2:1 to 1:10 were used. Altering the voltage pulses and the composition and temperature of the reaction gas initiates a first stage of growth of the compound surface layer or diffusion into the base material. A first stage reaction gas is introduced to the reaction vessel. For example, a reaction gas comprising 5-10% nitrogen and correspondingly 95-90% hydrogen. The reaction gas at this step may also contain small amounts of argon or carbon precursor. A partial vacuum with a pressure of less than 1 atmosphere and commonly of less than 100 mbars is maintained for the reaction gases and the temperature in the reaction vessel is maintained between approximately 400°C and approximately 600°C for approximately three to six hours. For the exemplary processing of femoral knee components, the reaction gas is introduced to the reaction vessel at a flow rate of approximately 150-300 liters per hour with a pressure of 1-10 mbars and the temperature is maintained at approximately 580°C for approximately four hours. To produce a first stage plasma, the reaction gas is excited with an electrical pulse typically at 450 to 550 volts with an on to off time ratio of approximately 1:2.

Depending on the desired surface layer or diffusion zone, the nitriding steps may be altered or repeated. Following initial growth of the surface layer or diffusion zone, the process variables may be revised to continue the growth of the surface layer and/or diffusion zone as required, or further control or minimize the diffusion of nitrogen into the component. A second stage reaction gas may comprise 5-10% nitrogen and correspondingly 95-90% other carrier gas, such as hydrogen. For example, the percentage of nitrogen in the reaction gas may be increased from 5% for the first stage of surface layer growth to 7.5% for second stage surface layer growth. Again, trace amounts of a carbon precursor may typically be included in the reaction gas

during the second stage of surface layer growth to stabilize the carbon concentration in the products or components being treated. A partial vacuum of less than 1 atmosphere is maintained in the reaction vessel during a second stage of surface layer growth. Additionally, the pulse voltage may be varied as required for processing. In the exemplary example of femoral knee components, the pulse voltage is reduced to approximately 480 volts. The skilled person will appreciate that the pulse voltage, the exposure duration of the part or component to plasma temperature, and the gas composition may all be varied as required to facilitate control of the surface layer to be grown as well as promote or suppress the development of the transition or diffusion layer or layers. In processing the exemplary load of femoral knee components, as example, the components are exposed to plasma of the second stage reaction gas for approximately 10-20 hours during the second stage of surface layer growth. The higher concentration of nitrogen in the reaction gas and lower pulse voltage and temperatures produces a second stage plasma that facilitates growth of the compound surface layer while permitting control to minimize or avoid the development of a diffusion layer.

The parts or components will be exposed to the plasma for sufficient time to permit the growth of the surface layer to reach a desired depth. For the exemplary load of moral knee components, this is typically three to fifteen microns. The skilled person will appreciate that the desired thickness of the compound layer and depth of the diffusion layer may vary with the particular parts or components to be treated and the application or use to be made of the particular alloy composition.

Step 80: On completion of the nitride steps, the temperature in the reaction vessel is reduced and the pressure is increased in preparation for removing the components from the reaction vessel. The parts are typically cooled down in the nitrogen atmosphere without plasma until sufficiently cool, such that no excessive oxidation will occur when exposed to ambient air. The cooling period may be for any number of hours as determined by the size of the load in the reaction vessel, the temperature in the reaction vessel being reduced to approximately 120°C and the pressure increased to approximately atmospheric. The process parts or components are then removed from the reaction vessel.

Step 90 and 100: The process components are then removed from the reaction vessel and a final finishing, typically limited to polishing for appearance is performed.

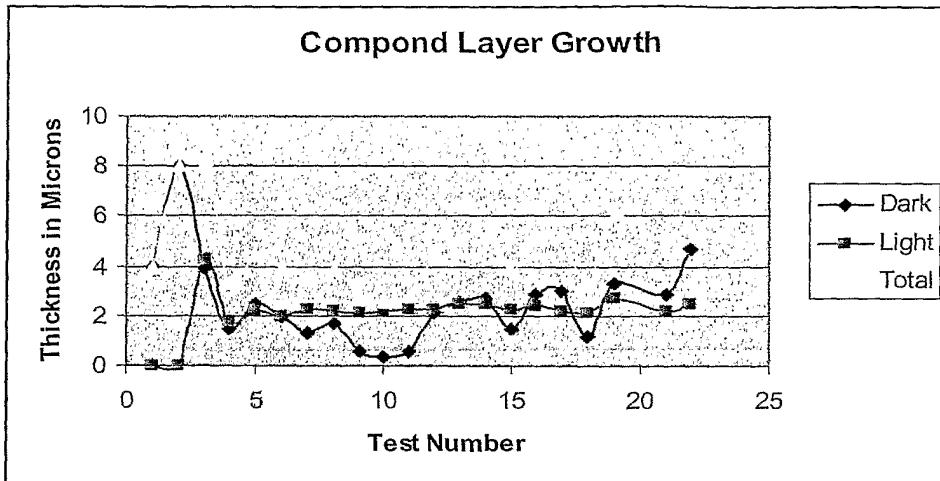
Referring to Figures 2 and 3, being micrographs, it is shown that the compound layer developed through two variations of the process. In Figure 2, the surface treatment process of the present invention caused a compound surface layer 2 to develop at the surface of a body of a cobalt-chromium alloy matrix. The surface layer is hard and smooth and subsumes particles of carbide, such as the particle 6 at the surface of the body 4 and seals over surface discontinuities. For the exemplary example of the aforesaid femoral knee component, analysis has confirmed that components of cobalt-chromium alloys subjected to the surface treatment of the process of the present invention develop a compound surface layer of approximately 3-15 microns thick. An analysis of the exemplary knee joint component also showed that the transition to the cobalt-chromium base metal of the body by way of the transition layer is approximately equal to the surface layer. From the exemplary example, the result is a medical device with a very smooth, hard, minimally abrasive surface that exhibits a very low coefficient friction and reduces wear of other material, such as polyethylene, they are commonly paired with cobalt chromium load bearing surfaces such as may be found in association with prosthetic devices.

Figure 3 is a micrograph showing two distinct phases 8 and 12 with the process of the present invention, the thickness of each phase is controllable through process variations.

Figure 4 is a calotest used to determine the compound layer thickness. Here it is further illustrated that two phases may be obtained in the compound layer.

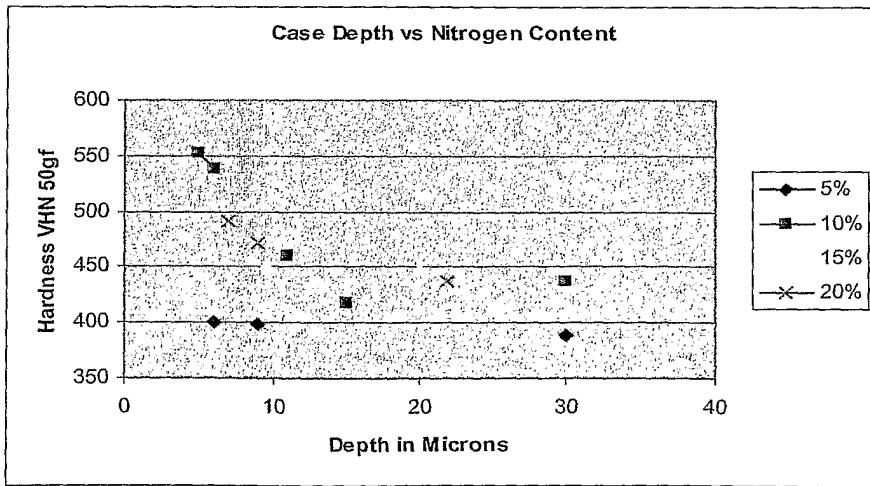
Graph 1 depicts compound layer growth with respect to variations in temperature, gas ratios, sputter step changes and exposure times. As can be seen, the ratio between the dark and light phases appearing in the compound layer as shown in Figure 4, can be controlled.

Graph 1:



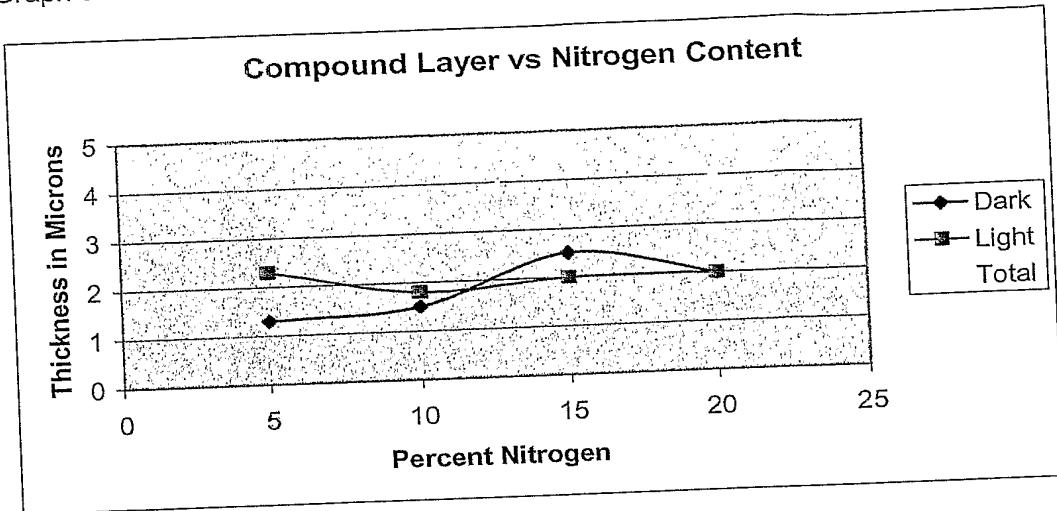
Graph 2 depicts the case depth in relation to the nitrogen content which provides the support for the hard compound layer for load bearing capability. Temperature, time and nitrogen content all have an effect, the following graph deals specifically with the nitrogen potential.

Graph 2:



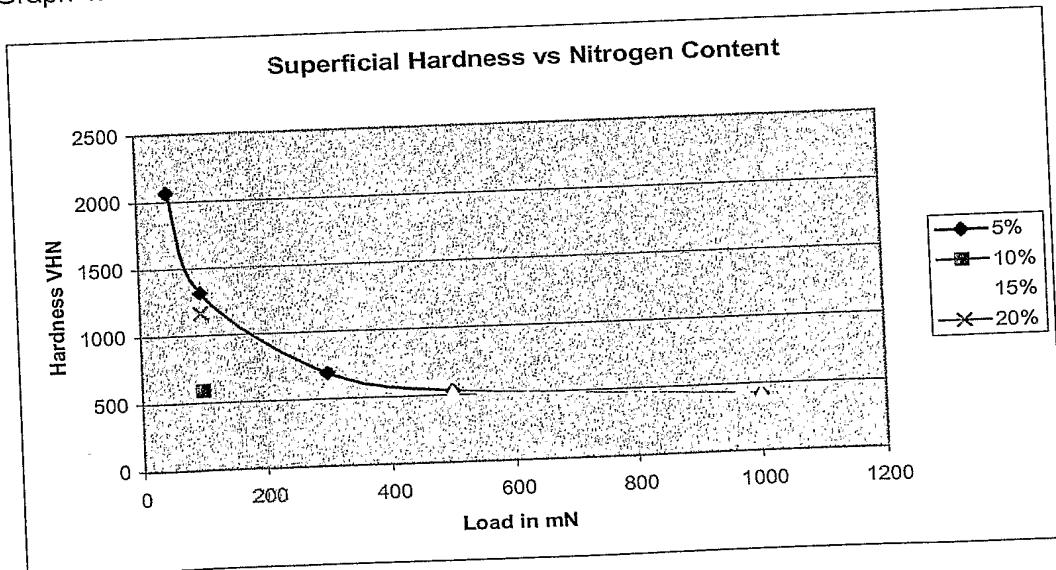
The compound layer thickness of each phase in relation to the nitrogen potential is illustrated in graph 3.

Graph 3:



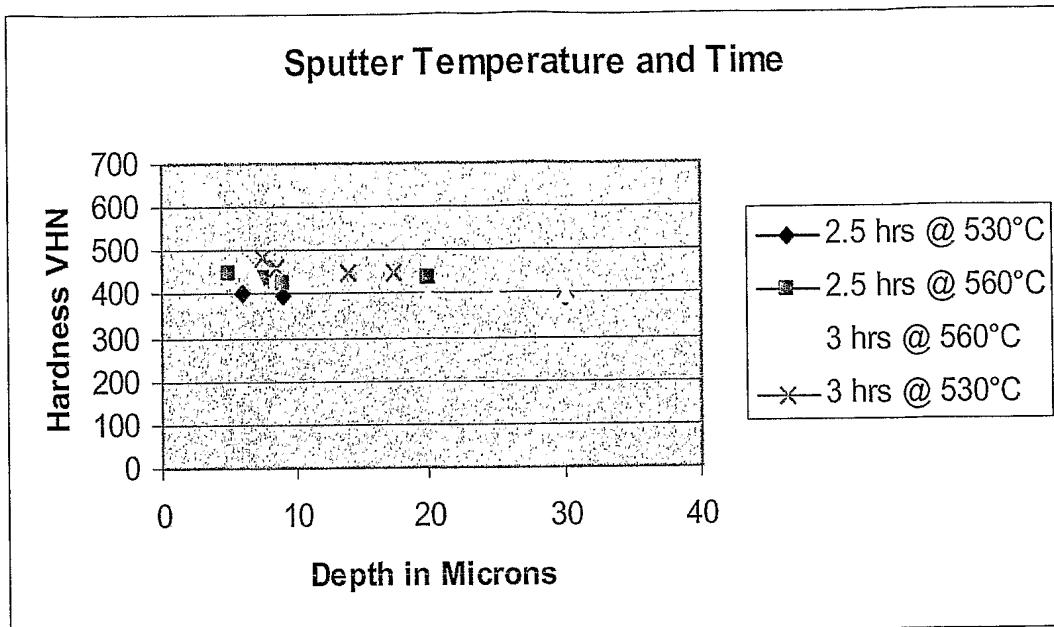
Graph shows the superficial hardness of the compound layer in relation to varying nitrogen potentials at increasing test loads.

Graph 4:

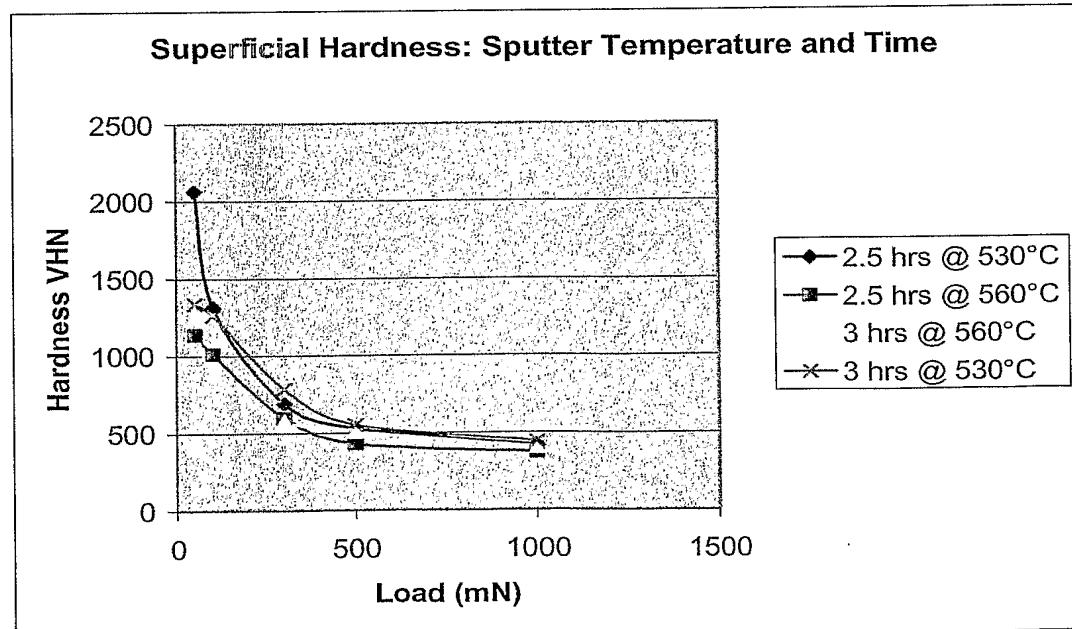


The effectiveness in creating an active surface beneficial for the nitriding process is depicted in graph 5 and 6 by variations of time and temperature in the sputter step on the case depth and superficial hardness. It was found that diffusion is related to time and temperature.

Graph 5:



Graph 6:



**Wear tests:**

A comparison between untreated and treated implants of the wear rate was determined using a tribometer pin on disk method. The average wear rate on untreated samples was found to be 0.2023 while the treated parts exhibited a wear rate of 0.1355. No discernable wear was noted on the treated alloy and 3D non-contact profilometry showed surface conditions of the alloy virtually unchanged.

**Rotating Beam Fatigue Testing:**

The following tables show the results in ascending load applications to treated (as per this invention) versus untreated control specimens. The data shows a clear increase in fatigue strength, control specimens exhibited failures at less than 10 million cycles with a 72.5 KSI load application while the treated ones did not exhibit failures at less than 10 million cycles until an 80 KSI load was applied.

**70 KSI Load**

Specimen ID	Cycles	Condition	Result
7680	12346600	Untreated	Discontinued
7682	10629100	Untreated	Discontinued
7696	10000800	Untreated	Discontinued

**72.5 KSI Load**

Specimen ID	Cycles	Condition	Result
7697	11789200	Untreated	Failed
7698	3560900	Untreated	Failed

**75 KSI Load**

Specimen ID	Cycles	Condition	Result
7679	5429100	Untreated	Failed
7695	3571400	Untreated	Failed
7675	10016500	Treated	Discontinued
7691	10341800	Treated	Discontinued
7693	10156600	Treated	Discontinued

**77.5 KSI Load**

Specimen ID	Cycles	Condition	Result
7694	16948400	Treated	Discontinued
7708	20887900	Treated	Discontinued

80 KSI

Specimen ID	Cycles	Condition	Result
7696	3287800	Treated	Failed
7677	8757800	Treated	Failed
7692	10116900	Treated	Discontinued

**What is Claimed**

1. A method for enhancing the surface hardness and smoothness of cobalt-chromium alloys through exposure in a reaction vessel to a mixture of reaction gases at a partial pressure (less than atmospheric) within a temperature range of 250°C to 1000°C for process time sufficient to create a substantial compound layer substantially comprising chromium nitride.
2. The method of claim 1 wherein the reaction vessel utilizes a pulse plasma glow discharge as a media for the reaction.
3. The method of claim 1 wherein the total pressure of reaction gases is 0.5 to 100 mbars.
4. The method of claim 1 where the temperature is 400°C to 600°C
5. The method of claim 1 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>.
6. The method of claim 3 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>.
7. The method of claim 1 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>.
8. The method of claim 3 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>.
9. The method of claim 1 wherein the reaction time is 6 – 42 hours
10. The method of claim 1 wherein the reaction time is approximately 24 hours.
11. The method of claim 1 where the pulse pause ratio is 1:0 to 1:50.
12. The method of claim 3 where the pulse pause ration is 5:1 to 1:20.
13. The method in claim 1 in which the identified hardened surface contains a compound layer of Cr-N of 1 to 20 microns thickness.
14. The method in claim 1 in which the identified hardened surface contains a compound layer of Cr-N of 3 to 15 microns thickness.
15. A method for enhancing the surface hardness and smoothness of a cobalt chromium material and with surface hardness and smoothness improved

through exposure in a reaction vessel to a mixture of reaction gases (Ar, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>) for process time sufficient to create a compound layer substantially comprised of chromium nitrides.

16. The method of claim 15 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>.
17. The method of claim 15 wherein the reaction gases are Ar, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>.
18. The method of claim 15 wherein the said material is ASTM F-75 and ASTM F-75 Modified alloy
19. The method of claim 15 wherein the process temperature is held between 400°C to 600°C.
20. The method of claim 15 wherein the process partial pressure is held at less than atmospheric.
21. The method of claim 15 wherein the process partial pressure is held at approximately 1-10 mbars.
22. The method of claim 15 wherein the said cobalt chromium alloy is ASTM F-799, F75, and F75 modified.
23. A method for enhancing the surface hardness and smoothness of a cobalt chromium molybdenum base material and with surface hardness and smoothness improved through exposure in a reaction vessel incorporating pulse plasma of reaction gases varies in on-to-off process levels.
24. The method of 15 and 24 where in the pulse plasma on-to-off ratio is 2:1 to 1:10.
25. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating convection preheating.
26. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating single and multi zone cooling
27. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating a central anode.

28. The method of 1, 3, and 15 through in a reaction vessel wherein the parts are masked to prevent nitriding in unwanted areas.
29. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating helium as a replacement carrier gas for the hydrogen.
30. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating thermocouple temperature measurement of the parts.
31. The method of 1, 3, and 15 through exposure in a reaction vessel incorporating a sputter step to increase the surface reactivity of the workpiece.
32. The method of any one of claims 15 to 31 wherein the creation of a substantial nitrogen diffusion layer is avoided.
33. The method of claim 1 wherein the reaction vessel utilizes a plasma glow discharge as a media for the reaction.
34. The method of claim 1 wherein the reaction gas is nitrogen.
35. The method of claim 1 wherein the reaction gases are nitrogen and a carrier gas with optionally argon and optionally a carbon precursor.

Figure 1:

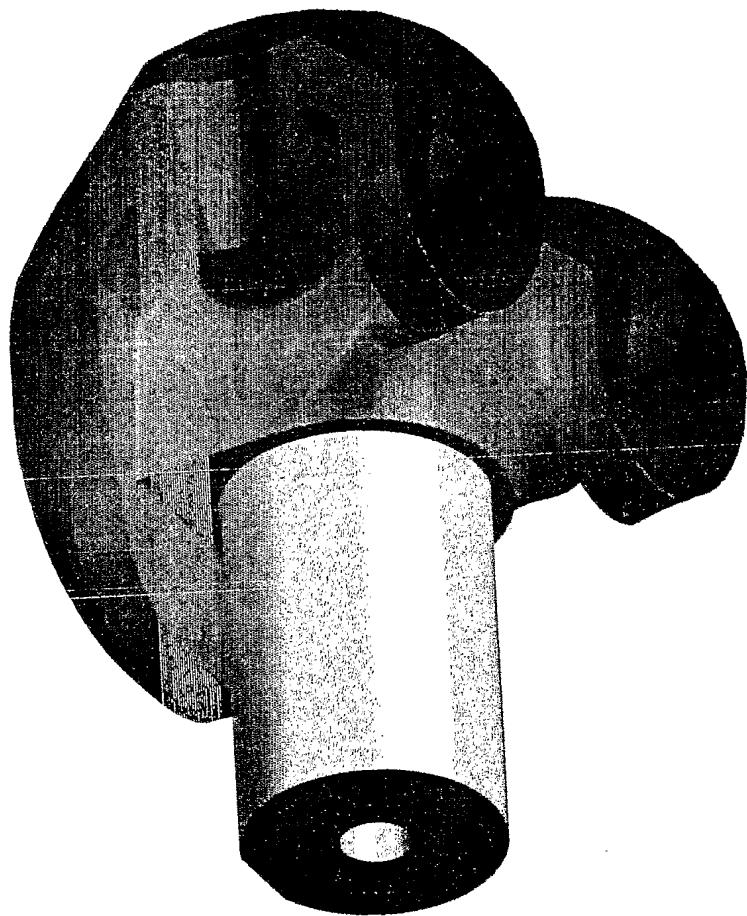
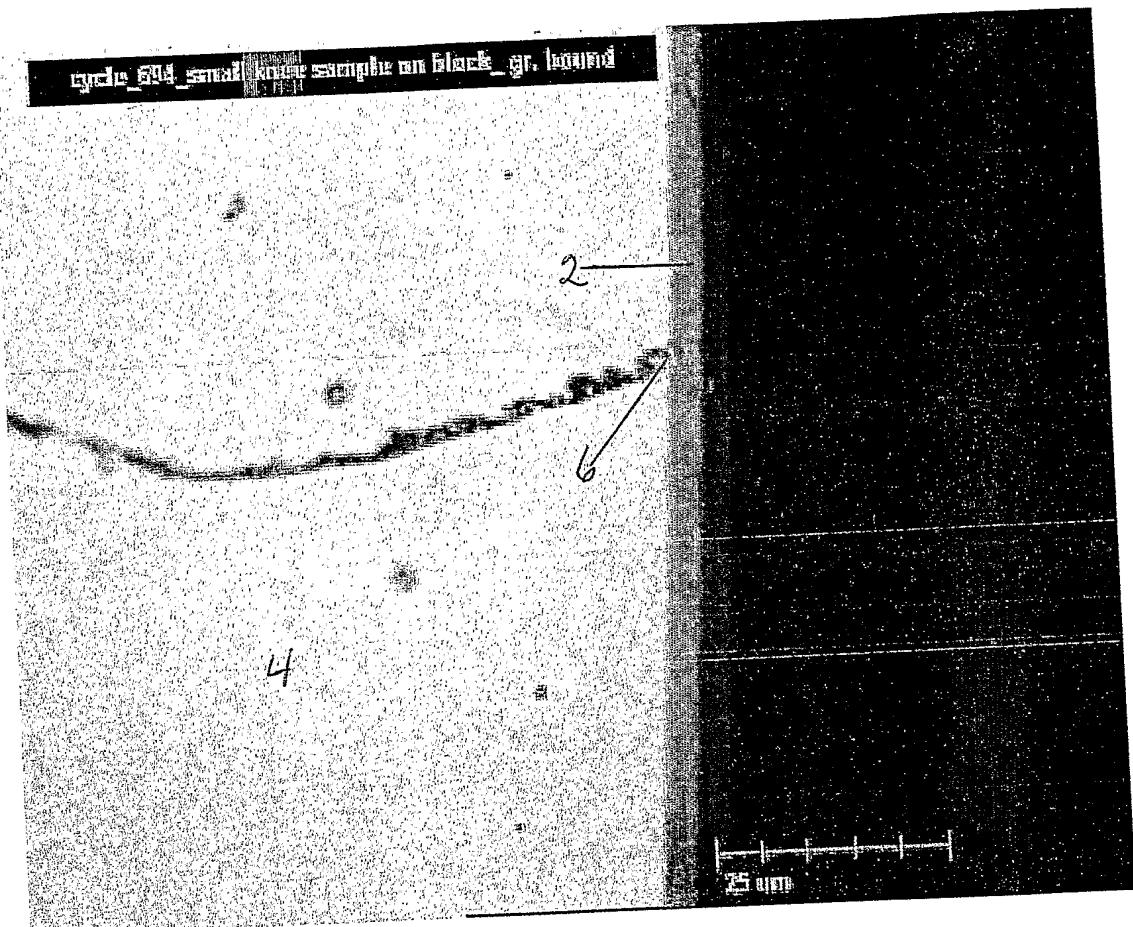
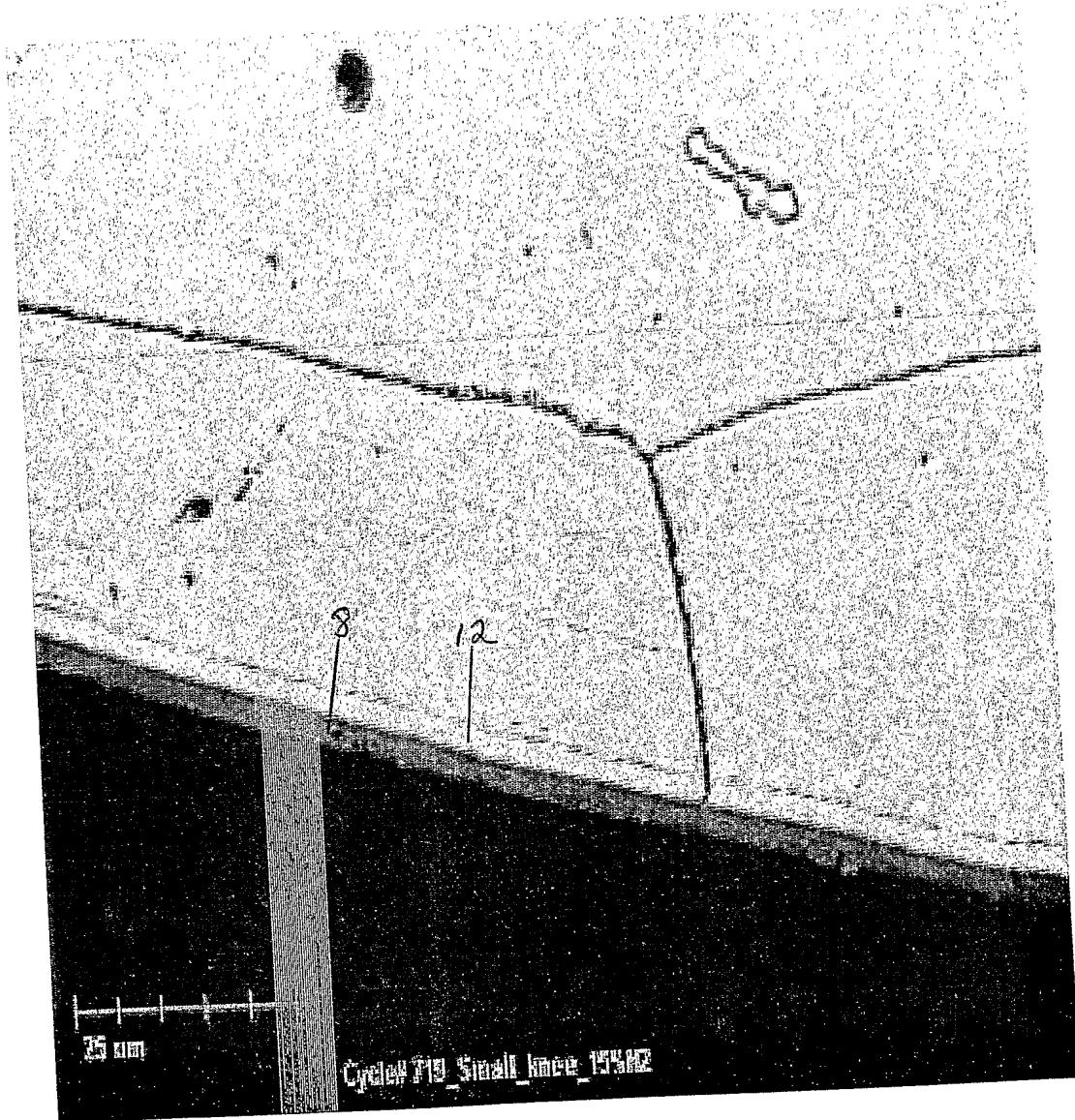


Figure 2



Micrograph 1, 1000X, Cycle 694

Figure 3



Micrograph 2, 1000X, Cycle 719

Figure 4



Micrograph, Cycle 730, Calotest

**Figure 5**